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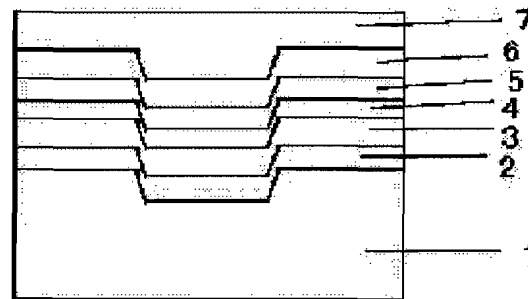
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(54) OPTICAL DATA RECORDING MEDIUM

(57)Abstract:

PROBLEM TO BE SOLVED: To realize an initialization-free medium, having a recording density of 4.7 GB/disc-120 mm-in-diameter or larger, which responds to high-speed overwrite recording, and is compatible with DVD-ROMs.

SOLUTION: An optical recording medium, having a recording layer including Sb and Te, in addition, substantially no other elements or at least one of elements of group 1 to group 7 in the periodic table and remnant layers is a phase-change recording medium, wherein the remnant layers include a material for speeding up linear velocity, and by a recording operation through energy irradiation to the optical data medium, the other elements in an amount existed in the recording layer at end of a deposition process of the recording layer or more are migrated from the remnant layers into the recording layer and exist there.



CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE
DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]When a layer of said the complementary carries out an energy ray to said optical information medium and carries out recording operation to it in an optical recording medium characterized by comprising the following including high linear velocity-ized material, A phase change recording medium with which said other elements of quantity of the more than which existed in this recording layer at the time of an end of a film production process of this recording layer shift into a recording layer, and come to exist from a layer of said the complementary. other elements other than Sb and Te are not included substantially — the [or / the Ith fellows of the periodic table thru/or] — a recording layer containing at least one kind of element of an element belonging to VII fellows.
A layer of the complementary.

[Claim 2]The phase change recording medium according to claim 1 with which said recording layer is characterized by Sb and being germanium content of 0 thru/or less than pentatomic % in an atomic number, including 1/3 or less Te of Sb.

[Claim 3]The phase change recording medium according to claim 1 or 2, wherein a layer of said the complementary is a crystallization promoting layer containing a recorded state stabilizing material and a crystallization accelerating material.

[Claim 4]The phase change recording medium according to claim 3, wherein said recorded state stabilizing materials are four group elements, 1B group element, three group elements, and/or five group elements.

[Claim 5]The phase change recording medium according to claim 4, wherein said recorded state stabilizing materials are germanium, Cu, In, B, and/or N.

[Claim 6]The phase change recording medium according to claim 3, wherein said high linear velocity-ized materials are Ga, Dy, Ca, Mg, and at least one element chosen from a group which consists of Mn.

[Claim 7]The phase change recording medium according to claim 6, wherein said high linear velocity-ized material is Ga or/and Mn.

[Claim 8]The phase change recording medium according to claim 3, wherein said crystallization accelerating materials are five group elements and six group elements.

[Claim 9]The phase change recording medium according to claim 8, wherein said crystallization accelerating materials are Sb, Bi, and/or Te.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]The initialization operation of this invention is unnecessary, it is excellent in preservation reliability, and relates to the optical information recording medium which can respond to high-speed over-writing record. It is applied to an optical disc.

[0002]

[Description of the Prior Art]By laser beam exposure, by record of information, reproduction, and an eliminable optical information recording medium and a laser beam exposure as an optical information recording medium in which record of information, reproduction, and elimination are possible. The commercialization as phase change CD-RW using the reversible phase change of a crystallized state and an amorphous (amorphous) state, DVD-RAM, -RW, +RW media, etc. is expected.

[0003]This invention persons have furthered research and development about what was constituted from a recording layer having a metastable Sb₃Te phase which belongs a recording layer to space group Fm3m among the above-mentioned phase change type optical information recording media (statements, such as JP,10-217069,A). This metastable phase differs from the recording layer of Sb-Te eutectic crystal structure, it does not separate into Sb and Sb₂Te₃, and disorder of the recording mark resulting from the grain boundary is not produced, either. Therefore, the thing using the recording layer having a metastable Sb₃Te phase belonging to space group Fm3m has the strong point whose high density recording becomes possible. Repeatedly, since it is strong to the thermal shock at the time of record, the recording layer having a metastable Sb₃Te phase belonging to space group Fm3m has the outstanding repetition recording characteristic.

[0004]By the way, in the phase change type optical information recording medium using the recording layer having a metastable Sb₃Te phase belonging to this space group Fm3m, a recording layer is produced by the vacuum producing-film methods, such as sputtering and vacuum evaporation, and the film immediately after film production has usually become an amorphous state. On the other hand, the recording layer of the optical information recording medium produced commercially must be a crystallized state. In the erasable light information record carrier using a phase transition, it is because record film is set as an amorphous state by a recorded state and is generally set as a crystallized state in the state of elimination (initialization). For this reason, the initialization process which heat-treats a laser beam exposure etc. and crystallizes a recording layer immediately after film production of a recording layer was required. However, since the time for 30 seconds or more is required for the above-mentioned initialization process, a throughput is downed, it is [many devices for an initialization process / stand] necessary for [when mass-producing], and an installation cost becomes expensive. As a result, the rise of product cost will be caused.

[0005]The recording layer which contains at least one kind of element of the element which belongs to the Ith fellows of the periodic table thru/or VII fellows other than Sb and Te excluding other elements substantially to such a problem, In the optical recording medium which has a layer of the complementary which consists of a crystallization promoting layer which consists of a crystallization accelerating material and a recorded state stabilizing material, Said other elements of the quantity of the more than which existed in this recording layer at the time of the end of stage film formation of this recording layer by carrying out an energy ray to said optical recording medium, and carrying out recording operation to it shift into a recording layer, and it is made to exist from the layer of said the complementary, There is art which made the initializing step unnecessary (the application-for-patent No. 319887 [2001 to] specification). However, while the use to high-density image recording expands a phase change recording medium in recent years, much more high-speed over-writing realization (7 which is 2-5X of the reproduction linear velocity of DVD-ROM - 17 m/s) has come to be required. Although the improvement (following, improvement in the speed) in the crystallization rate of the recording layer material in the time of mark elimination (the melting point near [i.e.,]) is needed for high-speed over-writing realization here, it is difficult to deal with such high-speed over-writing in said art. Because, according to the knowledge known until now, can attain improvement in the speed of recording layer material by making the compounding ratio of Sb high about the phase change type optical information recording medium (JP,2000-43415,A) which has a metastable Sb₃Te phase to which a recording layer belongs to space group Fm3m, but. Since the preservation reliability of a medium falls in connection with it, it is a practical level and is because the medium [over-write / medium / high-speed] cannot be provided.

[0006]

[Problem(s) to be Solved by the Invention]Therefore, the purpose of this invention cancels the above-mentioned problem, and there is in realizing the initialization loess media of the storage density of 120 or more mm disks of 4.7 GB / diameters in which the compatibility with DVD-ROM which can respond to high-speed over-writing record is possible.

[0007]

[Means for Solving the Problem]an aforementioned problem does not contain substantially other elements other than (1) "Sb of this invention, and Te -- the [or / the Ith fellows of the periodic table thru/or] -- in an optical recording medium which has a recording layer containing at least one kind of element of an element belonging to VII fellows, and a layer of the complementary, When a layer of said the complementary carries out an energy ray to said optical information medium and carries out recording operation to it including high linear velocity-ized material, "A phase change recording medium with which said other elements of quantity of the more than which existed in this recording layer at the time of an end of a film production process of this recording layer shift into a recording layer, and come to exist from a layer of said the complementary", and (2) Said recording layer Sb, A phase change recording medium given in said ** (1) paragraph characterized by being germanium content of 0 thru/or less than pentatomic % by an atomic number including 1/3 or less Te of Sb", -- (3) "phase change recording medium given in said ** (1) paragraph or a ** (2) paragraph, wherein a layer of said the complementary is a crystallization promoting layer containing a recorded state stabilizing material and a crystallization accelerating material". -- (4) "phase change recording medium given in said ** (3) paragraph, wherein said recorded state stabilizing materials are four group elements, 1B group element, three group elements, and/or five group elements", and (5) -- "said recorded state stabilizing material -- germanium, [Cu, In and] A phase change recording medium given in said ** (4) paragraph being B and/or N", -- (6) "phase change recording medium given in said ** (3) paragraph, wherein said high linear velocity-ized materials are Ga, Dy, Ca, Mg, and at least one element chosen from a group which consists of Mn". -- (7) "phase change recording medium given in said ** (6) paragraph, wherein said high linear velocity-ized material is Ga or/and Mn". (it is attained by 8) "phase change recording medium given in said ** (3) paragraph, wherein said crystallization accelerating materials are five group elements and six group elements", and (9) "a phase change recording medium given in said ** (8) paragraph, wherein said crystallization accelerating materials are Sb, Bi, and/or Te."

[0008]In an optical recording medium which has a recording layer containing at least one kind of element of an element which belongs to the Ith fellows of the periodic table thru/or VII fellows other than Sb and Te excluding other elements substantially, and a layer of the complementary,

Said other elements of quantity of the more than which existed in this recording layer at the time of an end of stage film formation of this recording layer by carrying out an energy ray to said optical recording medium, and carrying out recording operation to it shift into a recording layer, and it is made to exist from a layer of said the complementary. An aforementioned problem is solved by having made a layer of the complementary into a crystallization promoting layer containing a recorded state stabilizing material, a crystallization accelerating material, and high linear velocity-ized material.

[0009]

[Embodiment of the Invention] Hereafter, this invention is explained in detail. The feature of this invention is that the accessory constituent (this is also hereafter called "impurity") of the quantity of the more than which existed in the recording layer at the time of the end of stage film formation is a phase change recording medium which comes to exist in a recording layer by recording. It is a quantity contrastive with this accessory constituent, and means that Sb and Te in a recording layer maintain a Sb₃Te system presentation, and the recording material of a recording layer holds the quantitative ratio of the grade in which phase-number conversion is possible to an amorphous phase-crystal phase by a write-operation and erasing operation as Sb as the main ingredients in this invention, and Te. The impurity of the quantity of the more than which said impurity was spread [in the crystallization promoting layer] to the recording layer including the recorded state stabilizing material at the time of phase change record as an impurity, and existed in the recording layer at the time of the end of stage film formation comes to exist in a recording layer. Therefore, the recorded state stabilizing material which a recording material should include beforehand can be decreased.

[0010] In this invention, high linear velocity-ized material is included in a crystallization promoting layer as an impurity. High linear velocity-ized material has an effect which raises the crystallization rate of a recording material [/ near the melting point], and the high-speed over-writing realization (7 which is 2-5X of the reproduction linear velocity of DVD-ROM - 17 m/s) of it is attained. Since improvement in the speed of recording layer material can be attained without increasing the rate of Sb occupied to a recording layer by adding high linear velocity-ized material, the problem that preservation reliability will fall with improvement in the speed of recording layer material does not arise.

[0011] It is preferred to use the group Ga, Dy, Ca, Mg, and at least one element chosen from Mn as a high linear velocity-ized material. The effect of improvement in the speed of recording layer material is checked from the result in which these investigated the addition effect over the phase change type optical information recording medium which has a Sb₃Te phase about many elements on the periodic table.

[0012] a group — Ga and/or especially Mn are especially preferred. Although each of D(ies), Ca, and Mg can attain improvement in the speed, when it is made to contain so much, it has the problem of causing the fall of a repetition recording characteristic. Although Ga has the problem of causing the fall of a recording characteristic repeatedly like Dy, Ca, and Mg, it has the effect of raising a conservation characteristic. For this reason, stabilization of a recorded state can also be attained with improvement in the speed. On the other hand, although the effect that Mn raises a conservation characteristic is not like Ga, the fall of a recording characteristic is not caused [the case where it is made to contain so much]. By using Ga and/or Mn as a high linear velocity-ized material from these things, a repetitive characteristic is good and it is possible to realize the phase change recording medium in which the conservation characteristic was further excellent.

[0013] When using germanium as a recorded state stabilizing material included in a crystallization promoting layer, germanium which a recording material is made to contain may be less than pentatomic %. When germanium which a recording material is made to contain in a crystal recording layer in a Sb₃Te system recording layer is less than pentatomic %, crystallization temperature will be less than 160 **. When crystallization temperature is less than 160 **, formation of the crystal record film of 80% of relative reflectance is attained also in the membrane formation process below the plastic deformation temperature of a polycarbonate board by using a crystallization promoting layer. It is a recording material for crystal recording layer formation which germanium is less than three atom % more desirably, and does not contain germanium most desirably. Here, the case where germanium contained in a recording material is less than one atom % is defined as not containing germanium substantially. When germanium contained in a Sb₃Te system recording material is 3atom%, the crystallization temperature of the case of 147 ** and less than one atom % is 110 **. In the case of 147 ** former crystallization temperature, at least 67 ** of the above-mentioned polycarbonate board heat-resistant temperature becomes usable crystal record film by initialization loess. The relative reflectance is about 80%. Becoming a crystal film even whose substrate temperature of 67 ** is still more perfect in the case of 110 ** latter crystallization temperature, the relative reflectance will be not less than 83%.

[0014] Record equivalent to at least 0.1 micrometer of record mark length is possible by extracting the beam system of recording laser light in this invention, since the recording material is a Sb₃Te system recording material. As a recorded state stabilizing material in this invention, four group elements, 1B group element, and three group elements are effective. germanium is the most effective and also Cu, In, and B are effective. In addition, five fellows' N is also effective in recorded state stabilization. As a crystallization accelerating material, five group elements and six group elements are effective. In particular, Sb, Bi, and Te are effective.

[0015] A crystallization promoting layer contains one or more sorts of ***** of the above, a recorded state stabilizing material, a crystallization accelerating material, and high linear velocity-ized material. The layer which consists of 2 yuan, Bi and germanium, is the most preferred as a crystallization promoting layer. To a crystallization promoting layer, the further impurity element may be added for melting point adjustment etc. An usable material as an impurity element Ag, Cd, Ce, Co, Cr, Fe, H, Hg, Ir, K, La, Li, Mo, Na, nickel, O, P, Pb, Pd, Po, Pr, Pt, Pu, Rb, Rh, Ru, S, Se, Si, Sn, Sr, Th, Ti, Tl, U, Cl, Br, etc. are mentioned.

[0016] The above-mentioned crystallization promoting layer does not need to serve as a thin film [**** / completely] on a substrate. That is, in the case of about 1 nm, membrane formation thickness is the island shape of discontinuous a large number by mass membrane thickness. If membrane formation thickness increases, said islands will be connected and it will become a perfect thin film on a substrate. In this invention, said island shape is also called crystallization promoting layer in a microscopic meaning.

[0017] Next, an example of the optical information recording medium by this invention is shown in drawing 1. (1) is a substrate and (2) is the 1st dielectric layer and an organic protective layer by which, as for a reflection radiation layer and (7), the 2nd dielectric layer and (6) are provided [(3)] for a recording layer and (5) on a reflection radiation layer if needed in a crystallization promoting layer and (4). By a diagram, only the information board side of an optical information recording medium is shown. As for the material of a substrate, in almost all cases, polycarbonate is used. After substrate thickness forms the layer of drawing 1 in the case more than 1-mm thickness, and about 0.6-mm substrate, it is and, in more than 2.0-mm thickness, in the case of **0.3 mm and 1.0-mm thickness, the permissible error of the substrate thickness in this invention comes out of the case where paste other 0.6-mm boards together and it is referred to as about 1.2 mm, **0.2 mm in the case of **0.2 mm and 0.6-mm thickness. The slot is formed in the substrate and the depth is 200A - about 450A. The pitch of a slot is 0.74 micrometer when using it as DVD compatible media. If minuteness making of this pitch is carried out to about 0.3 micrometer, record of not less than 20 GB is possible on a disk 120 mm in radius by using the laser of blue light.

[0018] In this invention, as the 1st and 2nd dielectric layers, SiO_x, ZnO, SnO₂, aluminum₂O₃, TiO₂, Metallic oxides, such as In₂O₃, MgO, ZrO₂, and Ta₂O₅, Carbide, such as sulfides, such as nitrides, such as Si₃N₄, AlN, TiN, BN, and ZrN, ZnS, and TaS₄, SiC, TaC, B₄C, WC, TiC, and ZrC, is mentioned. Such materials can be alone used as a protective layer, and can also be used as a mixture. For example, ZnS, SiO_x, and Ta₂O₅ and SiO_x are mentioned as a mixture.

[0019] The thickness of the 1st dielectric layer has the preferred range of 50-250 nm. If it becomes thinner than 50 nm, it becomes the fall of an environment-resistant protection feature, a heat-resistant fall, and the fall of *****, and is not desirable. in the film production process by a sputtering technique etc. if it becomes thicker than 250 nm -- film temperature -- since film peeling and a crack arise by the rise of a degree or the fall of the sensitivity at the time of record is brought about, it is not desirable. As for the thickness of the 2nd dielectric layer, 15-50 nm is preferred. In the case of the 2nd dielectric layer, if thinner than 10 nm, heat resistance falls and it is not desirable. On the contrary, if 100 nm is exceeded, repetitive overwriting characteristics will worsen due to the fall of the film peeling by the fall of recording sensitivity, and a rise in heat, modification, and heat dissipation nature.

[0020] As a reflection radiation layer (6), the simple substance or alloy of material mainly concerned with metal, such as aluminum, Au, Cu, Ag, Cr,

Sr, Zn, In, Pd, Zr, Fe, Co, nickel, Si, germanium, Sb, Ta, W, Ti, and Pb, can be used. It is important for this layer to make heat radiate efficiently, and 50–160 nm of thickness is preferred. When thickness is too thick, radiation efficiency is too large, if sensitivity worsens and is too thin, sensitivity is good, but repetitive overwriting characteristics worsen. As the characteristic, thermal conductivity is high and it is required with a high-melting point that adhesion with the charge of a protective layer material should be good etc.

[0021]One in the case of pasting together to drawing 2 and using a substrate about 0.6 mm thick is shown. About dielectric materials, a crystallization accelerating material, a recording material, and the charge of a reflective radiating material, it is the same as that of the case of said drawing 1. In the case of drawing 2, transmissivity of the translucent reflection radiation layer of (13) and the 1st recording layer of (11) is made not less than 50%.

[0022]The case where it has a two-layer recording layer on a substrate about 1 mm thick is shown in drawing 3. About dielectric materials, a crystallization accelerating material, a recording material, and the charge of a reflective radiating material, it is the same as that of the case of said drawing 1. Since the transmissivity of the 1st recording layer is adjusted in the case of drawing 3, the 1st dielectric layer of (22) and the 2nd dielectric layer of (25) may be made into the multilayered constitution of a dissimilar material.

[0023]In order to carry out optical recording to the optical information recording medium of such this invention, when forming AMORUFASU equivalent to a reference clock length n cycle, laser pulse irradiation of a time $(n-1)$ is performed at the time of n cycle. For example, when forming AMORUFASU of the length of reference clock 5 cycle shown in drawing 4, it irradiates with 4 times of laser pulses. in recording-linear-velocity 8.5 m/s — the case (DVD.) of record with 63.7 MHz of reference clocks ** laser radiation start time delay in 2.4X record, for example, a figure, — 19 ns and ** leading pulse width — for 6 ns, for 7 ns, 15 mW and ** erase power are performed at 8 mW, and, as for ** multi-pulse width, ** cooling pulse width performs ** cooling power for ** record power at 0.1 mW for 14.5 ns.

[0024]For example, the above-mentioned material and the optical information recording medium by composition are the semiconductor lasers whose wavelength is 635 or 650 nm, and record reproduction can be carried out using the pickup of NA0.6. As a record method, a modulation code can use EFM or an EFM+ [8 / 16RLL (2, 10)] method by Pulse Width Modulation, for example. In this case, a pulse is divided into the multi-pulse part of a leading pulse and after that. A multi-pulse part is for repeating heating and cooling and performing them. In this case, the relation of each power serves as heating (record) power > erase power > cooling power, and cooling power is lowered to a read-out power grade. Usually, linear velocity is performed by 3.5 – 8.5 m/s, and read-out power is performed at 1 mW or less.

[0025]

[Example]Hereafter, this invention is explained based on an example. The thin film of the following (1) – (5) is formed by sputtering process on 0.6-mm thickness and a polycarbonate board (the following, PC board) 5 inches in diameter.

(1) Dielectric layer:ZnS-SiO₂ which is the 1st (being a mol ratio of a target 79.5:20.5); 220 nm of thickness.

(2) Crystallization promoting layer : the target which consists of a recorded state stabilizing material, a crystallization accelerating material, and high linear velocity-ized material was used. A presentation and thickness are shown in Table 1.

(3) Recording layer : **** for alloy targets of Sb₃Te system material. A presentation is shown in Table 1. 16 nm of thickness.

(4) Dielectric layer:ZnS-SiO₂ which is the 2nd (being a mol% ratio of a target 79.5:20.5); 10 nm of thickness.

(5) reflection radiation layer: — AlTi; — 140 nm of thickness.

Substrate temperature at the time of recording layer membrane formation was performed at the temperature of the limit in which a polycarbonate board does not carry out plastic deformation. In this case, IR lamp output is controlled so that the thermo couple contacted to the substrate will be 100 **, and after monitor temperature with a thermoelectrical object is stabilized, the substrate is conveyed in the recording layer membrane formation room. It was 67 ** when the substrate temperature in the recording layer membrane formation room was measured. After the end of membrane formation, after carrying out the spin coat of the UV curing resin, curing formation was carried out by UV light exposure. Thus, the manufactured substrate was pasted together to other 0.6-mm boards in thickness, and was made into about 1.2-mm thickness.

[0026]The wavelength of 660 nm and the pickup head of NA0.65 were used, and an equivalent for the storage density set to 4.7 GB on diameter 120 mm disk with recording linear velocity 8.5 and the speed of 14 m/s was recorded. Also when writing one mark, it recorded with the multipulse system which repeats laser radiation and cooling. Although the amorphous mark of the length of the multiple of clock 1 cycle was formed, laser radiation of the same number of times as the pitch of the clock per mark length and cooling were performed. The ratio of the laser radiation power at the time of amorphous mark formation (record power) to the power at the time of crystal space formation (erase power) differs in an optimum value with the thickness and material of a crystallization promoting layer, and are (record power)/(erase power) = 0.4 – 0.6.

[0027]A jitter is the value which ** (ed) standard deviation of gap of the reading time of the boundary of a recording mark and a space by read clock 1 period time among a recording characteristic (unit %), and modulation is the value which ** (ed) amplitude of 14T with the reflectance of 14T.

[0028](Examples 1–8, comparative examples 1–2) About Examples 1–8 and the comparative examples 1–2. The media reflectance immediately after manufacture and relative reflectance, recording linear velocity 8.5, the repetition record jitter properties evaluated by speed (an equivalent for 2.5 or 4X linear velocity DVD) of 14 m/s, and time for a record jitter to go up 1% at the time of 80 ** storage were evaluated. The result is shown in Table 2. Relative reflectance serves as a rule of thumb of the crystallization percentage of completion in a film production stage, and is defined by the following formulas here.

[0029]

[Equation 1]Relative reflectance =(media reflectance before record)/(reflectance of melting recrystallization formed at time of record) x100 (%)

[0030]And since according to the knowledge which the artificer acquired media reflectance is changed with record as this is less than 80%, the good media characteristic is not obtained.

[0031]As a result of evaluating, about Examples 1–8, the media reflectance could secure not less than 20%, and the relative reflectance could secure not less than 80%, and the endurance time of 100 hours could be secured as preservation reliability, and preservation reliability was good. The first time and the 1000 times record of recording linear velocity 8.5 and the repetition record jitter properties in the speed of 14 m/s are less than 10%.

The good characteristic was shown.

[0032]On the other hand, although preservation reliability was good, the repetition record jitter properties in recording-linear-velocity 8.5 m/s are less than 10% and the first time and 1000 times record showed the good characteristic in the comparative example 1, The first time and 1000 times record were over 15%, and the repetition record jitter properties in the recording linear velocity of 14 m/s were the very bad characteristic. Since there is no high linear velocity-ized material, this is considered because improvement in the speed of a recording material is insufficient.

[0033]In the comparative example 2, recording linear velocity 8.5 and the repetition record jitter properties in the speed of 14 m/s had dramatically bad preservation reliability, although the first time and 1000 times record are less than 10% and showed the good characteristic. Since the rate of Sb was increased for improvement in the speed of recording layer material and preservation reliability fell, this is considered.

[0034]

[Table 1]

	結晶化促進層材料	結晶化促進層膜厚/nm	記録層材料	混合後組成 / atom%				
				Bi	Ge	X	Sb	Te
比較例1	BiGe	2.0	Sb80Te20	4.4	6.6	0	71.2	17.8
比較例2	BiGe	2.0	Sb86Te14	4.4	6.6	0	76.5	12.5
実施例1	BiGeGa	2.0	Sb80Te20	3.7	3.7	Ga:3.7	71.2	17.8
実施例2	BiGeGa	2.0	Sb80Te20	4.4	3.3	Ga:3.3	71.2	17.8
実施例3	BiGeDy	2.0	Sb80Te20	3.7	3.7	Dy:3.7	71.2	17.8
実施例4	BiGeMg	2.0	Sb80Te20	3.7	3.7	Mg:3.7	71.2	17.8
実施例5	BiGeCa	2.0	Sb80Te20	3.7	3.7	Ca:3.7	71.2	17.8
実施例6	BiGeGa	1.5	Ge2Sb78Te20	4	4.3	Ga:2.2	71.2	18.3
実施例7	BiGeMn	2.0	Sb80Te20	3.7	3.7	Mn:3.7	71.2	17.8
実施例8	BiGeGaMn	2.0	Sb80Te20	3.3	3.3	Ga:2.2 Mn:2.2	71.2	17.8

[0035]
[Table 2]

	製造直後のメディア反射率 ／相対反射率	80℃保管時に記録ジッターが 1%上昇する時間	初回記録ノダイレクトオーバーライト1000 回目のジッター（記録線速85m/s)	初回記録ノダイレクトオーバーライト1000 回目のジッター（記録線速14m/s)
比較例1	20% / 83%	100時間以上	10%未満 / 10%未満	15%以上 / 15%以上
比較例2	20% / 82%	5時間未満	10%未満 / 10%未満	10%未満 / 10%未満
実施例1	20% / 81%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満
実施例2	20% / 85%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満
実施例3	20% / 83%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満
実施例4	20% / 83%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満
実施例5	20% / 83%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満
実施例6	20% / 81%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満
実施例7	20% / 83%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満
実施例8	20% / 81%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満

[0036]
[Effect of the Invention]As mentioned above, initialization loess manufacture of a Sb₃Te system recording material phase change archive medium is enabled by this invention so that clearly from detailed and concrete explanation, The extremely outstanding effect that the initialization loess media of the storage density of 120 or more mm disks of 4.7 GB / diameters in which compatibility with DVD-ROM is possible are realizable is done so.

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TECHNICAL FIELD

[Field of the Invention]The initialization operation of this invention is unnecessary, it is excellent in preservation reliability, and relates to the optical information recording medium which can respond to high-speed over-writing record.
It is applied to an optical disc.

[Translation done.]

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PRIOR ART

[Description of the Prior Art]By laser beam exposure, by record of information, reproduction, and an eliminable optical information recording medium and a laser beam exposure as an optical information recording medium in which record of information, reproduction, and elimination are possible. The commercialization as phase change CD-RW using the reversible phase change of a crystallized state and an amorphous (amorphous) state, DVD-RAM, -RW, +RW media, etc. is expected.

[0003]This invention persons have furthered research and development about what was constituted from a recording layer having a metastable Sb₃Te phase which belongs a recording layer to space group Fm3m among the above-mentioned phase change type optical information recording media (statements, such as JP,10-217069,A). This metastable phase differs from the recording layer of Sb-Te eutectic crystal structure, it does not separate into Sb and Sb₂Te₃, and disorder of the recording mark resulting from the grain boundary is not produced, either. Therefore, the thing using the recording layer having a metastable Sb₃Te phase belonging to space group Fm3m has the strong point whose high density recording becomes possible. Repeatedly, since it is strong to the thermal shock at the time of record, the recording layer having a metastable Sb₃Te phase belonging to space group Fm3m has the outstanding repetition recording characteristic.

[0004]By the way, in the phase change type optical information recording medium using the recording layer having a metastable Sb₃Te phase belonging to this space group Fm3m, a recording layer is produced by the vacuum producing-film methods, such as sputtering and vacuum evaporation, and the film immediately after film production has usually become an amorphous state. On the other hand, the recording layer of the optical information recording medium produced commercially must be a crystallized state. In the erasable light information record carrier using a phase transition, it is because record film is set as an amorphous state by a recorded state and is generally set as a crystallized state in the state of elimination (initialization). For this reason, the initialization process which heat-treats a laser beam exposure etc. and crystallizes a recording layer immediately after film production of a recording layer was required. However, since the time for 30 seconds or more is required for the above-mentioned initialization process, a throughput is downed, it is [many devices for an initialization process / stand] necessary for [when mass-producing], and an installation cost becomes expensive. As a result, the rise of product cost will be caused.

[0005]The recording layer which contains at least one kind of element of the element which belongs to the Ith fellows of the periodic table thru/or VII fellows other than Sb and Te excluding other elements substantially to such a problem, In the optical recording medium which has a layer of the complementary which consists of a crystallization promoting layer which consists of a crystallization accelerating material and a recorded state stabilizing material, Said other elements of the quantity of the more than which existed in this recording layer at the time of the end of stage film formation of this recording layer by carrying out an energy ray to said optical recording medium, and carrying out recording operation to it shift into a recording layer, and it is made to exist from the layer of said the complementary, There is art which made the initializing step unnecessary (the application-for-patent No. 319887 [2001 to] specification). However, while the use to high-density image recording expands a phase change recording medium in recent years, much more high-speed over-writing realization (7 which is 2-5X of the reproduction linear velocity of DVD-ROM - 17 m/s) has come to be required. Although the improvement (following, improvement in the speed) in the crystallization rate of the recording layer material in the time of mark elimination (the melting point near [i.e.,]) is needed for high-speed over-writing realization here, it is difficult to deal with such high-speed over-writing in said art. Because, according to the knowledge known until now, can attain improvement in the speed of recording layer material by making the compounding ratio of Sb high about the phase change type optical information recording medium (JP,2000-43415,A) which has a metastable Sb₃Te phase to which a recording layer belongs to space group Fm3m, but. Since the preservation reliability of a medium falls in connection with it, it is a practical level and is because the medium [over-write / medium / high-speed] cannot be provided.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention]As mentioned above, initialization loess manufacture of a Sb_3Te system recording material phase change archive medium is enabled by this invention so that clearly from detailed and concrete explanation, The extremely outstanding effect that the initialization loess media of the storage density of 120 or more mm disks of 4.7 GB / diameters in which compatibility with DVD-ROM is possible are realizable is done so.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]Therefore, the purpose of this invention cancels the above-mentioned problem, and there is in realizing the initialization loess media of the storage density of 120 or more mm disks of 4.7 GB / diameters in which the compatibility with DVD-ROM which can respond to high-speed over-writing record is possible.

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MEANS

[Means for Solving the Problem] An aforementioned problem does not contain substantially other elements other than (1) "Sb of this invention, and Te — the [or / the lth fellows of the periodic table thru/or] — in an optical recording medium which has a recording layer containing at least one kind of element of an element belonging to VII fellows, and a layer of the complementary, When a layer of said the complementary carries out an energy ray to said optical information medium and carries out recording operation to it including high linear velocity-ized material, "A phase change recording medium with which said other elements of quantity of the more than which existed in this recording layer at the time of an end of a film production process of this recording layer shift into a recording layer, and come to exist from a layer of said the complementary", and (2) Said recording layer Sb, A phase change recording medium given in said ** (1) paragraph characterized by being germanium content of 0 thru/or less than pentatomic % by an atomic number including 1/3 or less Te of Sb", (— 3) "phase change recording medium given in said ** (1) paragraph or a ** (2) paragraph, wherein a layer of said the complementary is a crystallization promoting layer containing a recorded state stabilizing material and a crystallization accelerating material". (— 4) "phase change recording medium given in said ** (3) paragraph, wherein said recorded state stabilizing materials are four group elements, 1B group element, three group elements, and/or five group elements", and (5) — "— said recorded state stabilizing material — germanium, [Cu, In and] A phase change recording medium given in said ** (4) paragraph being B and/or N", (— 6) "phase change recording medium given in said ** (3) paragraph, wherein said high linear velocity-ized materials are Ga, Dy, Ca, Mg, and at least one element chosen from a group which consists of Mn". (— 7) "phase change recording medium given in said ** (6) paragraph, wherein said high linear velocity-ized material is Ga or/and Mn". (it is attained by 8) "phase change recording medium given in said ** (3) paragraph, wherein said crystallization accelerating materials are five group elements and six group elements", and (9) "a phase change recording medium given in said ** (8) paragraph, wherein said crystallization accelerating materials are Sb, Bi, and/or Te."

[0008] In an optical recording medium which has a recording layer containing at least one kind of element of an element which belongs to the lth fellows of the periodic table thru/or VII fellows other than Sb and Te excluding other elements substantially, and a layer of the complementary, Said other elements of quantity of the more than which existed in this recording layer at the time of an end of stage film formation of this recording layer by carrying out an energy ray to said optical recording medium, and carrying out recording operation to it shift into a recording layer, and it is made to exist from a layer of said the complementary, An aforementioned problem is solved by having made a layer of the complementary into a crystallization promoting layer containing a recorded state stabilizing material, a crystallization accelerating material, and high linear velocity-ized material.

[0009]

[Embodiment of the Invention] Hereafter, this invention is explained in detail. The feature of this invention is that the accessory constituent (this is also hereafter called "impurity") of the quantity of the more than which existed in the recording layer at the time of the end of stage film formation is a phase change recording medium which comes to exist in a recording layer by recording. It is a quantity contrastive with this accessory constituent, and means that Sb and Te in a recording layer maintain a Sb₃Te system presentation, and the recording material of a recording layer holds the quantitative ratio of the grade in which phase-number conversion is possible to an amorphous phase-crystal phase by a write-operation and erasing operation as Sb as the main ingredients in this invention, and Te. The impurity of the quantity of the more than which said impurity was spread [in the crystallization promoting layer] to the recording layer including the recorded state stabilizing material at the time of phase change record as an impurity, and existed in the recording layer at the time of the end of stage film formation comes to exist in a recording layer. Therefore, the recorded state stabilizing material which a recording material should include beforehand can be decreased.

[0010] In this invention, high linear velocity-ized material is included in a crystallization promoting layer as an impurity. High linear velocity-ized material has an effect which raises the crystallization rate of a recording material [/ near the melting point], and the high-speed over-writing realization (7 which is 2-5X of the reproduction linear velocity of DVD-ROM - 17 m/s) of it is attained. Since improvement in the speed of recording layer material can be attained without increasing the rate of Sb occupied to a recording layer by adding high linear velocity-ized material, the problem that preservation reliability will fall with improvement in the speed of recording layer material does not arise.

[0011] It is preferred to use the group Ga, Dy, Ca, Mg, and at least one element chosen from Mn as a high linear velocity-ized material. The effect of improvement in the speed of recording layer material is checked from the result in which these investigated the addition effect over the phase change type optical information recording medium which has a Sb₃Te phase about many elements on the periodic table.

[0012] a group — Ga and/or especially Mn are especially preferred. Although each of D(ies), Ca, and Mg can attain improvement in the speed, when it is made to contain so much, it has the problem of causing the fall of a repetition recording characteristic. Although Ga has the problem of causing the fall of a recording characteristic repeatedly like Dy, Ca, and Mg, it has the effect of raising a conservation characteristic. For this reason, stabilization of a recorded state can also be attained with improvement in the speed. On the other hand, although the effect that Mn raises a conservation characteristic is not like Ga, the fall of a recording characteristic is not caused [the case where it is made to contain so much]. By using Ga and/or Mn as a high linear velocity-ized material from these things, a repetitive characteristic is good and it is possible to realize the phase change recording medium in which the conservation characteristic was further excellent.

[0013] When using germanium as a recorded state stabilizing material included in a crystallization promoting layer, germanium which a recording material is made to contain may be less than pentatomic %. When germanium which a recording material is made to contain in a crystal recording layer in a Sb₃Te system recording layer is less than pentatomic %, crystallization temperature will be less than 160 **. When crystallization temperature is less than 160 **, formation of the crystal record film of 80% of relative reflectance is attained also in the membrane formation process below the plastic deformation temperature of a polycarbonate board by using a crystallization promoting layer. It is a recording material for crystal recording layer formation which germanium is less than three atom % more desirably, and does not contain germanium most desirably. Here, the case where germanium contained in a recording material is less than one atom % is defined as not containing germanium substantially. When germanium contained in a Sb₃Te system recording material is 3atom%, the crystallization temperature of the case of 147 ** and less than one atom % is 110 **. In the case of 147 ** former crystallization temperature, at least 67 ** of the above-mentioned polycarbonate board heat-resistant temperature becomes usable crystal record film by initialization loess. The relative reflectance is about 80%. Becoming a crystal film even whose substrate temperature of 67 ** is still more perfect in the case of 110 ** latter crystallization temperature, the relative reflectance will be not less than 83%.

[0014] Record equivalent to at least 0.1 micrometer of record mark length is possible by extracting the beam system of recording laser light in this invention, since the recording material is a Sb₃Te system recording material. As a recorded state stabilizing material in this invention, four group elements, 1B group element, and three group elements are effective. germanium is the most effective and also Cu, In, and B are effective. In addition, five fellows' N is also effective in recorded state stabilization. As a crystallization accelerating material, five group elements and six group elements are effective. In particular, Sb, Bi, and Te are effective.

[0015] A crystallization promoting layer contains one or more sorts of ***** of the above, a recorded state stabilizing material, a crystallization accelerating material, and high linear velocity-ized material. The layer which consists of 2 yuan, Bi and germanium, is the most preferred as a crystallization promoting layer. To a crystallization promoting layer, the further impurity element may be added for melting point adjustment etc. An usable material as an impurity element Ag, Cd, Ce, Co, Cr, Fe, H, Hg, Ir, K, La, Li, Mo, Na, nickel, O, P, Pb, Pd, Po, Pr, Pt, Pu, Rb, Rh, Ru, S, Se, Si, Sn, Sr, Th, Ti, Tl, U, Cl, Br, etc. are mentioned.

[0016] The above-mentioned crystallization promoting layer does not need to serve as a thin film [**** / completely] on a substrate. That is, in the case of about 1 nm, membrane formation thickness is the island shape of discontinuous a large number by mass membrane thickness. If membrane formation thickness increases, said islands will be connected and it will become a perfect thin film on a substrate. In this invention, said island shape is also called crystallization promoting layer in a microscopic meaning.

[0017] Next, an example of the optical information recording medium by this invention is shown in drawing 1. (1) is a substrate and (2) is the 1st dielectric layer and an organic protective layer by which, as for a reflection radiation layer and (7), the 2nd dielectric layer and (6) are provided [(3)] for a recording layer and (5) on a reflection radiation layer if needed in a crystallization promoting layer and (4). By a diagram, only the information board side of an optical information recording medium is shown. As for the material of a substrate, in almost all cases, polycarbonate is used. After substrate thickness forms the layer of drawing 1 in the case more than 1-mm thickness, and about 0.6-mm substrate, it is and, in more than 2.0-mm thickness, in the case of **0.3 mm and 1.0-mm thickness, the permissible error of the substrate thickness in this invention comes out of the case where paste other 0.6-mm boards together and it is referred to as about 1.2 mm, **0.2 mm in the case of **0.2 mm and 0.6-mm thickness. The slot is formed in the substrate and the depth is 200A – about 450A. The pitch of a slot is 0.74 micrometer when using it as DVD compatible media. If minuteness making of this pitch is carried out to about 0.3 micrometer, record of not less than 20 GB is possible on a disk 120 mm in radius by using the laser of blue light.

[0018] In this invention, as the 1st and 2nd dielectric layers, SiOx, ZnO, SnO₂, aluminum₂O₃, TiO₂, Metallic oxides, such as In₂O₃, MgO, ZrO₂, and Ta₂O₅, Carbide, such as sulfides, such as nitrides, such as Si₃N₄, AlN, TiN, BN, and ZrN, ZnS, and TaS₄, SiC, TaC, B₄C, WC, TiC, and ZrC, is mentioned. Such materials can be alone used as a protective layer, and can also be used as a mixture. For example, ZnS, SiOx, and Ta₂O₅ and SiOx are mentioned as a mixture.

[0019] The thickness of the 1st dielectric layer has the preferred range of 50–250 nm. If it becomes thinner than 50 nm, it becomes the fall of an environment-resistant protection feature, a heat-resistant fall, and the fall of *****, and is not desirable. in the film production process by a sputtering technique etc. if it becomes thicker than 250 nm — film temperature — since film peeling and a crack arise by the rise of a degree or the fall of the sensitivity at the time of record is brought about, it is not desirable. As for the thickness of the 2nd dielectric layer, 15–50 nm is preferred. In the case of the 2nd dielectric layer, if thinner than 10 nm, heat resistance falls and it is not desirable. On the contrary, if 100 nm is exceeded, repetitive overwriting characteristics will worsen due to the fall of the film peeling by the fall of recording sensitivity, and a rise in heat, modification, and heat dissipation nature.

[0020] As a reflection radiation layer (6), the simple substance or alloy of material mainly concerned with metal, such as aluminum, Au, Cu, Ag, Cr, Sr, Zn, In, Pd, Zr, Fe, Co, nickel, Si, germanium, Sb, Ta, W, Ti, and Pb, can be used. It is important for this layer to make heat radiate efficiently, and 50–160 nm of thickness is preferred. When thickness is too thick, radiation efficiency is too large, if sensitivity worsens and is too thin, sensitivity is good, but repetitive overwriting characteristics worsen. As the characteristic, thermal conductivity is high and it is required with a high-melting point that adhesion with the charge of a protective layer material should be good etc.

[0021] One in the case of pasting together to drawing 2, and using a substrate about 0.6 mm thick is shown. About dielectric materials, a crystallization accelerating material, a recording material, and the charge of a reflective radiating material, it is the same as that of the case of said drawing 1. In the case of drawing 2, transmissivity of the translucent reflection radiation layer of (13) and the 1st recording layer of (11) is made not less than 50%.

[0022] The case where it has a two-layer recording layer on a substrate about 1 mm thick is shown in drawing 3. About dielectric materials, a crystallization accelerating material, a recording material, and the charge of a reflective radiating material, it is the same as that of the case of said drawing 1. Since the transmissivity of the 1st recording layer is adjusted in the case of drawing 3, the 1st dielectric layer of (22) and the 2nd dielectric layer of (25) may be made into the multilayered constitution of a dissimilar material.

[0023] In order to carry out optical recording to the optical information recording medium of such this invention, when forming AMORUFASU equivalent to a reference clock length n cycle, laser pulse irradiation of a time (n–1) is performed at the time of n cycle. For example, when forming AMORUFASU of the length of reference clock 5 cycle shown in drawing 4, it irradiates with 4 times of laser pulses. in recording-linear-velocity 8.5 m/s — the case (DVD.) of record with 63.7 MHz of reference clocks ** laser radiation start time delay in 2.4X record, for example, a figure, — 19 ns and ** leading pulse width — for 6 ns, for 7 ns, 15 mW and ** erase power are performed at 8 mW, and, as for ** multi-pulse width, ** cooling pulse width performs ** cooling power for ** record power at 0.1 mW for 14.5 ns.

[0024] For example, the above-mentioned material and the optical information recording medium by composition are the semiconductor lasers whose wavelength is 635 or 650 nm, and record reproduction can be carried out using the pickup of NA0.6. As a record method, a modulation code can use EFM or an EFM+ [8 / 16RLL (2, 10)] method by Pulse Width Modulation, for example. In this case, a pulse is divided into the multi-pulse part of a leading pulse and after that. A multi-pulse part is for repeating heating and cooling and performing them. In this case, the relation of each power serves as heating (record) power > erase power > cooling power, and cooling power is lowered to a read-out power grade. Usually, linear velocity is performed by 3.5 – 8.5 m/s, and read-out power is performed at 1 mW or less.

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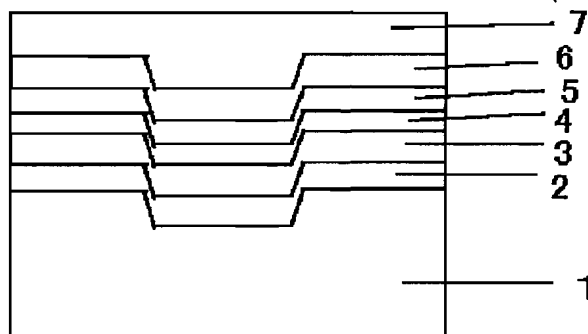
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(54) 【発明の名称】 光情報記録媒体

(57) 【要約】

【課題】 高速オーバーライト記録に対応できる、DVD-ROM互換が可能な4. 7GB/直径120mmディスク以上の記録密度の初期化レスメディアを実現すること。

【解決手段】 Sb、Teの他に、他元素を実質的に含まない又は周期律表第I族乃至第VII族に属する元素の少なくとも1種類の元素を含む記録層と、その余の層とを有する光記録媒体において、前記その余の層が高線速化材料を含み、前記光情報媒体にエネルギー照射して記録操作することにより、該記録層の製膜工程終了時に該記録層中に存在した以上の量の前記他元素が前記その余の層から記録層中に移行して存在するようになる相変化記録媒体。



【特許請求の範囲】

【請求項 1】 Sb、Te の他に、他元素を実質的に含まない又は周期律表第 I 族乃至第 VII 族に属する元素の少なくとも 1 種類の元素を含む記録層と、その余の層とを有する光記録媒体において、前記その余の層が高線速化材料を含み、前記光情報媒体にエネルギー照射して記録操作することにより、該記録層の製膜工程終了時に該記録層中に存在した以上の量の前記他元素が前記その余の層から記録層中に移行して存在するようになる相変化記録媒体。

【請求項 2】 前記記録層が、Sb と、原子数で Sb の $1/3$ 以下の Te とを含み、且つ 0 乃至 5 原子%未満の Ge 含有量であることを特徴とする請求項 1 に記載の相変化記録媒体。

【請求項 3】 前記その余の層が、記録状態安定化材料と結晶化促進材料とを含む結晶化促進層であることを特徴とする請求項 1 又は 2 に記載の相変化記録媒体。

【請求項 4】 前記記録状態安定化材料が、4 族元素、1 B 族元素、3 族元素及び／又は 5 族元素であることを特徴とする請求項 3 に記載の相変化記録媒体。

【請求項 5】 前記記録状態安定化材料が、Ge、Cu、In、B 及び／又は N であることを特徴とする請求項 4 に記載の相変化記録媒体。

【請求項 6】 前記高線速化材料が Ga、Dy、Ca、Mg、Mn からなる群から選ばれた少なくとも一つの元素であることを特徴とする請求項 3 に記載の相変化記録媒体。

【請求項 7】 前記高線速化材料が Ga または／及び Mn であることを特徴とする請求項 6 に記載の相変化記録媒体。

【請求項 8】 前記結晶化促進材料が、5 族元素、6 族元素であることを特徴とする請求項 3 に記載の相変化記録媒体。

【請求項 9】 前記結晶化促進材料が、Sb、Bi 及び／又は Te であることを特徴とする請求項 8 に記載の相変化記録媒体。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、初期化操作が不要で、保存信頼性に優れ、高速オーバーライト記録に対応できる光情報記録媒体に関するものであり、光ディスクに応用される。

【0002】

【従来の技術】 レーザビーム照射により情報の記録、再生及び消去が可能な光情報記録媒体とレーザビーム照射により情報の記録、再生及び消去が可能な光情報記録媒体として、結晶状態と非晶質（アモルファス）状態の可逆的相変化を利用した相変化 CD-RW、DVD-RAM、-RW、+RW メディアなどとしての商品化が期待されている。

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【0003】 本発明者等は、上記相変化型光情報記録媒体のうち、記録層を空間群 Fm3m に属する準安定 Sb3Te 相を有することを特徴とする記録層で構成したものについて研究、開発を進めてきた（特開平 10-217069 号公報等記載）。この準安定相は Sb-Te 共晶構造の記録層とは異なっており、Sb と Sb2Te3 とに分離せず、結晶粒界に起因する記録マークの乱れも生じない。そのため、空間群 Fm3m に属する準安定 Sb3Te 相を有することを特徴とする記録層を用いたものは、高密度記録が可能となる長所を持っている。さらに、空間群 Fm3m に属する準安定 Sb3Te 相を有することを特徴とする記録層は繰り返し記録時の熱衝撃に強いので、優れた繰り返し記録特性を有している。

【0004】 ところで、この空間群 Fm3m に属する準安定 Sb3Te 相を有することを特徴とする記録層を用いた相変化型光情報記録媒体では、記録層はスパッタリング、蒸着などの真空製膜法で製膜され、製膜直後の膜は、通常、非晶質状態となっている。一方、製品化された光情報記録媒体の記録層は結晶状態でなければならない。なぜなら、相転移を利用する書き換え型の光情報記録担体では、一般に記録膜が記録状態では非晶質状態に、消去（初期化）状態では結晶状態に設定されるからである。このため、記録層の製膜直後に、レーザビーム照射などの熱処理を施して記録層を結晶化させる初期化プロセスが必要であった。しかしながら、上記初期化プロセスには 30 秒以上の時間が必要であるため、スループットがダウンし、量産を行なう場合には初期化プロセスのための装置が多数台必要となり、設備費が高価になる。その結果、製品コストの上昇を招くことになる。

【0005】 こうした問題に対して、Sb、Te の他に、他元素を実質的に含まない又は周期律表第 I 族乃至 VII 族に属する元素の少なくとも 1 種類の元素を含む記録層と、結晶化促進材料と記録状態安定化材料からなる結晶化促進層からなる、その余の層とを有する光記録媒体において、前記光記録媒体にエネルギー照射して記録操作することにより、該記録層の成膜工程終了時に該記録層中に存在した以上の量の前記他元素が前記その余の層から記録層中に移行して存在するようにして、初期化工程を不要とした技術がある（特願 2001-319887 号明細書）。しかしながら、近年、相変化記録媒体は高密度画像記録への用途が拡大するとともに、より一層の高速オーバーライト実現（DVD-ROM の再生線速の 2～5 倍速である $7 \sim 17 \text{ m/s}$ ）が要求されるようになってきた。ここで、高速オーバーライト実現には、マーク消去時、すなわち融点近傍における記録層材料の結晶化速度の向上（以下、高速化）が必要となるが、前記技術では、そのような高速オーバーライトに対応することが困難である。なぜならば、これまで知られている知見によると、記録層が空間群 Fm3m に属する準安定 Sb3Te 相を有する相変化型光情報記録媒体

(特開2000-43415号公報)については、Sbの配合比を高くすることにより記録層材料の高速化は図れるが、それにともない媒体の保存信頼性が低下してしまうため、実用的なレベルで、高速オーバーライト可能な媒体を提供することができないからである。

【0006】

【発明が解決しようとする課題】従って、本発明の目的は、上記問題点を解消し、高速オーバーライト記録に対応できるDVD-ROM互換が可能な4.7GB/直径120mmディスク以上の記録密度の初期化レスメディアを実現することにある。

【0007】

【課題を解決するための手段】上記課題は、本発明の

(1)「Sb、Teの他に、他元素を実質的に含まない又は周期律表第I族乃至第VII族に属する元素の少なくとも1種類の元素を含む記録層と、その余の層とを有する光記録媒体において、前記その余の層が高線速化材料を含み、前記光情報媒体にエネルギー照射して記録操作することにより、該記録層の製膜工程終了時に該記録層中に存在した以上の量の前記他元素が前記その余の層から記録層中に移行して存在するようになる相変化記録媒体」、(2)「前記記録層が、Sbと、原子数でSbの1/3以下のTeとを含み、且つ0乃至5原子%未満のGe含有量であることを特徴とする前記第(1)項に記載の相変化記録媒体」、(3)「前記その余の層が、記録状態安定化材料と結晶化促進材料とを含む結晶化促進層であることを特徴とする前記第(1)項又は第(2)項に記載の相変化記録媒体」、(4)「前記記録状態安定化材料が、4族元素、1B族元素、3族元素及び/又は5族元素であることを特徴とする前記第(3)項に記載の相変化記録媒体」、(5)「前記記録状態安定化材料が、Ge、Cu、In、B及び/又はNであることを特徴とする前記第(4)項に記載の相変化記録媒体」、(6)「前記高線速化材料がGa、Dy、Ca、Mg、Mnからなる群から選ばれた少なくとも一つの元素であることを特徴とする前記第(3)項に記載の相変化記録媒体」、(7)「前記高線速化材料がGaまたは/及びMnであることを特徴とする前記第(6)項に記載の相変化記録媒体」、(8)「前記結晶化促進材料が、5族元素、6族元素であることを特徴とする前記第(3)項に記載の相変化記録媒体」、(9)「前記結晶化促進材料が、Sb、Bi及び/又はTeであることを特徴とする前記第(8)項に記載の相変化記録媒体」により達成される。

【0008】Sb、Teの他に、他元素を実質的に含まない又は周期律表第I族乃至第VII族に属する元素の少なくとも1種類の元素を含む記録層と、その余の層とを有する光記録媒体において、前記光記録媒体にエネルギー照射して記録操作することにより、該記録層の成膜工程終了時に該記録層中に存在した以上の量の前記他元素が

前記その余の層から記録層中に移行して存在するようにし、その余の層を記録状態安定化材料と結晶化促進材料と高線速化材料とを含む結晶化促進層としたことにより、上記課題を解決したものである。

【0009】

【発明の実施の形態】以下、本発明を詳細に説明する。本発明の特徴は、記録することにより、成膜工程終了時に記録層に存在した以上の量の副成分(以下、これを「不純物」とも云う)が記録層に存在するようになる相変化記録媒体であることである。本発明における主成分としてのSb、Teとは、該副成分と対照的な量であり、記録層中のSb及びTeがSb₃Te系組成を維持し且つ記録層の記録材料が書込操作及び消去操作によりアモルファス相-結晶相に相変換可能な程度の量比を保持することを意味する。結晶化促進層に不純物として記録状態安定化材料を含み、相変化記録時に前記不純物が記録層へと拡散し成膜工程終了時に記録層に存在した以上の量の不純物が記録層に存在するようになる。そのため、あらかじめ記録材料が含むべき記録状態安定化材料を減少させることができる。

【0010】さらに、本発明では、結晶化促進層に不純物として高線速化材料を含む。高線速化材料は、融点近傍における記録材料の結晶化速度を高める効果を有するものであり、高速オーバーライト実現(DVD-ROMの再生線速の2~5倍速である7~17m/s)が可能となる。なお、高線速化材料を加えることにより、記録層に占めるSbの割合を増やすことなく、記録層材料の高速化を図れるため、記録層材料の高速化にともなって保存信頼性が低下してしまうという問題が生じない。

【0011】高線速化材料としては、一群Ga、Dy、Ca、Mg、Mnの中から選ばれる少なくとも一つの元素を用いることが好ましい。これらは、Sb₃Te相を有する相変化型光情報記録媒体に対する添加効果を周期律表上の数多くの元素について調べた結果から、記録層材料の高速化の効果が確認されたものである。

【0012】なお、一群の中でもGaおよび/またはMnが特に好ましい。Dy、Ca、Mgはいずれも高速化は図れるものの、多量に含有させた場合、繰り返し記録特性の低下をきたすという問題を有している。Gaは、Dy、Ca、Mgと同様に繰り返し記録特性の低下をきたすという問題を有しているものの、保存特性を向上させる効果を有している。このため、高速化とともに記録状態の安定化も図ることができる。一方、Mnは、保存特性を向上させる効果はGaほどではないが、多量に含有させた場合でも繰り返し記録特性の低下をきたすことがない。これらのことから、高線速化材料としてGaおよび/またはMnを用いることにより、繰り返し特性が良く、保存特性がさらに優れた相変化記録媒体を実現することが可能である。

【0013】結晶化促進層に含む記録状態安定化材料と

してGeを用いる場合、記録材料に含有させるGeは5原子%未満で良い。Sb3Te系記録層において結晶記録層において記録材料に含有させるGeが5原子%未満の場合、結晶化温度が160℃未満となる。結晶化温度が160℃未満の場合は、結晶化促進層を用いることによりポリカーボネート基板の塑性変形温度以下の成膜プロセスでも相対反射率80%の結晶記録膜の形成が可能となる。結晶記録層形成のためのより望ましくはGeが3原子%未満であり、最も望ましくはGeを含有しない記録材料である。ここで、記録材料中に含まれるGeが1原子%未満の場合をGeを実質的に含有しないと定義する。Sb3Te系記録材料に含まれるGeが3原子%の場合、結晶化温度は147℃、1原子%未満の場合は110℃である。前者結晶化温度147℃の場合、前述のポリカーボネート基板耐熱温度の67℃でも初期化レスで使用可能な結晶記録膜となる。その相対反射率は80%程度である。後者結晶化温度110℃の場合は、基板温度67℃でも更に完全な結晶膜となり、その相対反射率は83%以上となる。

【0014】本発明では、記録材料がSb3Te系記録材料であることから、記録レーザー光のビーム系を絞ることにより少なくとも0.1μmの記録マーク長に相当する記録までは可能である。本発明における記録状態安定化材料としては、4族元素、1B族元素、3族元素が有効である。Geが最も有効である他、Cu、In、Bも有効である。加えて、5族のNも記録状態安定化に有効である。結晶化促進材料としては、5族元素、6族元素が有効である。特に、Sb、Bi、Teが有効である。

【0015】結晶化促進層は、上記、記録状態安定化材料と結晶化促進材料と高線速化材料とのそれぞれ1種以上を含有する。結晶化促進層として最も好ましいのは、BiとGeの2元からなる層である。更に、結晶化促進層には、融点調整等のために更なる不純物元素を添加する場合もある。不純物元素として使用可能な材料は、Ag、Cd、Ce、Co、Cr、Fe、H、Hg、Ir、K、La、Li、Mo、Na、Ni、O、P、Pb、Pd、Po、Pr、Pt、Pu、Rb、Rh、Ru、S、Se、Si、Sn、Sr、Th、Ti、Tl、U、ClおよびBr等が挙げられる。

【0016】上記結晶化促進層は基板上で完全に連続な薄膜とならなくても良い。すなわち、成膜膜厚が質量膜厚で1nm程度の場合は、不連続な多数の島状になっている。成膜膜厚が増加すると、前記島同士がつながり、基板上で完全な薄膜となる。本発明においては、前記島状をも微視的な意味で結晶化促進層という。

【0017】次に、本発明による光情報記録媒体の一例を図1に示す。(1)が基板、(2)が第1の誘電体層、(3)が結晶化促進層、(4)が記録層、(5)が第2の誘電体層、(6)が反射放熱層、(7)は必要に

応じて反射放熱層の上に設けられる有機保護層である。なお、図では、光情報記録媒体の情報基板側のみを示している。基板の材料は、ほとんどの場合ポリカーボネートが使用される。基板厚さは、1mm厚以上の場合と、約0.6mmの基板に図1の層を形成した後、他の0.6mm基板を貼り合わせて約1.2mmとする場合があり、本発明における基板厚の許容誤差は、2.0mm厚以上の場合±0.3mm、1.0mm厚の場合±0.2mm、0.6mm厚の場合±0.2mm、である。基板には、溝が形成してあり、その深さは200Å~450Å程度である。溝のピッチはDVD互換メディアとして使用する場合0.74μmである。このピッチを、0.3μm程度まで微細化すると、青色発光のレーザーを使うことにより、半径120mmのディスク上で20GB以上の記録が可能である。

【0018】本発明において、第1および第2の誘電体層としては、SiO_x、ZnO、SnO₂、Al₂O₃、TiO₂、In₂O₃、MgO、ZrO₂、Ta₂O₅等の金属酸化物、Si₃N₄、AlN、TiN、BN、ZrN等の窒化物、ZnS、Ta₂S₅等の硫化物、SiC、TaC、B₄C、WC、TiC、ZrC等の炭化物が挙げられる。これらの材料は、単体で保護層として用いることができ、また、混合物として用いることもできる。例えば、混合物としては、ZnSとSiO_x、Ta₂O₅とSiO_xが挙げられる。

【0019】第1の誘電体層の膜厚は、50~250nmの範囲が好ましい。50nmより薄くなると、耐環境性保護機能の低下、耐熱性低下、蓄熱効果の低下となり好ましくない。250nmより厚くなると、スパッタ法等による製膜過程において、膜温度の上昇により膜剥離やクラックが生じたり、記録時の感度の低下をもたらすので好ましくない。第2の誘電体層の膜厚は15~50nmが好ましい。第2の誘電体層の場合、10nmより薄いと耐熱性が低下し好ましくない。逆に、100nmを越えると、記録感度の低下、温度上昇による膜剥離、変形、放熱性の低下により、繰り返しオーバーライト特性が悪くなる。

【0020】反射放熱層(6)としては、Al、Au、Cu、Ag、Cr、Sr、Zn、In、Pd、Zr、Fe、Co、Ni、Si、Ge、Sb、Ta、W、Ti、Pb等の金属を主とした材料の単体または合金を用いることができる。この層は、熱を効率的に放散させることが重要であり、膜厚は50~160nmが好ましい。膜厚が厚すぎると、放熱効率が大きすぎて感度が悪くなり、薄すぎると感度は良好であるが、繰り返しオーバーライト特性が悪くなる。特性としては、熱伝導率が高く、高融点で保護層材料との密着性がよいことなどが要求される。

【0021】図2に、厚さ約0.6mmの基板を貼り合わせて使用する場合の1例を示す。誘電体材料、結晶化

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促進材料、記録材料、反射放熱材料については、前記図1の場合と同様である。図2の場合では、(13)の半透明反射放熱層及び、(11)の第1の記録層の透過率を50%以上にする。

【0022】図3に、厚さ1mm程度の基板の上に、2層の記録層を有する場合を示す。誘電体材料、結晶化促進材料、記録材料、反射放熱材料については、前記図1の場合と同様である。図3の場合、第1の記録層の透過率を調節するため、(22)の第1の誘電体層及び(25)の第2の誘電体層を異種材料の多層構成とする場合がある。

【0023】このような本発明の光情報記録媒体に光記録するには、基準クロック長さ n 周期に相当するアモルファスを形成する場合、 n 周期の時間に $(n-1)$ 回のレーザーパルス照射を行なう。例えば、図4に示す基準クロック5周期相当の長さのアモルファスを形成する場合は、4回のレーザーパルスを照射する。記録線速度8.5m/sにおいて、基準クロック63.7MHzでの記録の場合(DVD、2.4倍速記録)、例えば図における、①レーザー照射開始遅延時間は19ns、②先頭パルス幅は6ns、③マルチパルス幅は7ns、④冷却パルス幅は14.5ns、⑤記録パワーは15mW、⑥消去パワーは8mW、⑦冷却パワーは0.1mWにて行なう。

【0024】上記材料および構成による光情報記録媒体は、例えば、波長が635あるいは650nmの半導体レーザーで、NA0.6のピックアップを用い記録再生することができる。記録方法としては、例えば、Pulse Width Modulationで変調コードがEFM又はEFM+[8/16RL(2,10)]方式等を用いることができる。この場合、パルスは先頭パルスとその後のマルチパルス部に分かれる。マルチパルス部は、加熱、冷却を繰り返し行なうためのものである。この場合、各パワーの関係は、加熱(記録)パワー>消去パワー>冷却パワーとなっていて、冷却パワーは読み出しパワー程度まで下げる。通常、線速は3.5~8.5m/s、読み出しパワーは1mW以下で行なう。

【0025】

【実施例】以下、本発明を実施例に基づき説明する。

0.6mm厚、直径5インチのポリカーボネート基板(以下、PC基板)上にスパッタリング法により以下の(1)~(5)の薄膜を形成する。

(1)第1の誘電体層:ZnS・SiO₂(ターゲットのmol比で79.5:20.5);膜厚220nm。

(2)結晶化促進層:記録状態安定化材料、結晶化促進材料、高線速化材料からなるターゲットを用いた。組成及び膜厚は表1に示す。

(3)記録層:Sb₃Te系材料の合金ターゲットを用いた。組成は表1に示す。膜厚16nm。

(4)第2の誘電体層:ZnS・SiO₂(ターゲット

のmol比で79.5:20.5);膜厚10nm。

(5)反射放熱層:AlTi;膜厚140nm。

記録層成膜時の基板温度は、ポリカーボネート基板が塑性変形しない限界の温度で行なった。この場合、基板に接触させた熱電対が100℃となるようにIRランプ出力を制御して、熱電体によるモニター温度が安定した後、基板を記録層成膜室に搬送している。記録層成膜室での、基板温度を測定すると67℃であった。成膜終了後、UV硬化樹脂をスピンコートした後、UV照射により硬化形成させた。このようにして製造した基板を、他の厚さ0.6mm基板と貼り合わせて約1.2mm厚とした。

【0026】波長660nm、NA0.65のピックアップヘッドを使用して、記録線速度8.5、14m/sの速さで、直径120mmディスク上で4.7GBとなる記録密度相当の記録を行なった。1つのマークを書く際にも、レーザー照射と冷却を繰り返すマルチパルス方式で記録を行なった。クロック1周期の倍数の長さのアモルファスマークを形成するのであるが、マーク長あたりのクロックの振動数と同一の回数のレーザー照射と冷却を行なった。アモルファスマーク形成時のレーザー照射パワー(記録パワー)と、結晶スペース形成時のパワー(消去パワー)の比は、結晶化促進層の膜厚及び材料により最適値が異なり、(記録パワー)/(消去パワー)=0.4~0.6である。

【0027】記録特性中、ジッターは、記録マークとスペースの境界の読み出し時間のズレの標準偏差を、読み出しクロック1周期時間で除した値であり(単位%)、モジュレーションは、14Tの振幅を14Tの反射率で除した値である。

【0028】(実施例1~8、比較例1~2)実施例1~8、比較例1~2について、製造直後のメディア反射率および相対反射率、記録線速度8.5、14m/sの速さ(線速DVD2.5、4倍速相当)で評価した繰り返し記録ジッター特性、80℃保管時に記録ジッターが1%上昇する時間を評価した。その結果を表2に示す。なお、ここで相対反射率とは、製膜段階での結晶化進行度の目安となるものであり、以下の式で定義される。

【0029】

【数1】相対反射率=(記録前のメディア反射率)/(記録時に形成される熔融再結晶の反射率)×100(%)

【0030】そして発明者が得た知見によると、これが80%未満であると、メディア反射率が記録とともに変動するため、良好なメディア特性が得られない。

【0031】評価した結果、実施例1~8については、メディア反射率は20%以上、相対反射率は80%以上を確保でき、また保存信頼性としては100時間の耐久時間を確保できており、保存信頼性が良好であった。またさらに、記録線速度8.5、14m/sの速さでの繰り返し記録ジッター特性は、初回、1000回記録ともに

10%未満であり、良好な特性を示した。

【0032】これに対して、比較例1においては、保存信頼性が良好であり、記録線速度8.5m/sでの繰り返し記録ジッタ特性は、初回、1000回記録ともに10%未満であり、良好な特性を示したが、14m/sの記録線速度での繰り返し記録ジッタ特性は初回、1000回記録ともに15%を越えており、非常に悪い特性であった。これは、高線速化材料がないため、記録材料の高線速化が不十分なためと思われる。

*

	結晶化促進層材料	結晶化促進層膜厚/nm	記録層材料	混合後組成 / atom%				
				Bi	Ge	X	Sb	Te
比較例1	BiGe	2.0	Sb80Te20	4.4	6.6	0	71.2	17.8
比較例2	BiGe	2.0	Sb86Te14	4.4	6.6	0	76.5	12.5
実施例1	BiGeGa	2.0	Sb80Te20	3.7	3.7	Ga:3.7	71.2	17.8
実施例2	BiGeGa	2.0	Sb80Te20	4.4	3.3	Ga:3.3	71.2	17.8
実施例3	BiGeDy	2.0	Sb80Te20	3.7	3.7	Dy:3.7	71.2	17.8
実施例4	BiGeMg	2.0	Sb80Te20	3.7	3.7	Mg:3.7	71.2	17.8
実施例5	BiGeCa	2.0	Sb80Te20	3.7	3.7	Ca:3.7	71.2	17.8
実施例6	BiGeGa	1.5	Ge2Sb78Te20	4	4.3	Ga:2.2	71.2	18.3
実施例7	BiGeMn	2.0	Sb80Te20	3.7	3.7	Mn:3.7	71.2	17.8
実施例8	BiGeGaMn	2.0	Sb80Te20	3.3	3.3	Ga:2.2 Mn2.2	71.2	17.8

【0035】

※ ※ 【表2】

	製造直後のメディア反射率 ／相対反射率	80℃保管時に記録ジッターが 1%上昇する時間	初回記録／ダイレクトオーバーライト1000 回目のジッター（記録線速8.5m/s）	初回記録／ダイレクトオーバーライト1000 回目のジッター（記録線速14m/s）
比較例1	20% / 83%	100時間以上	10%未満 / 10%未満	15%以上 / 15%以上
比較例2	20% / 82%	5時間未満	10%未満 / 10%未満	10%未満 / 10%未満
実施例1	20% / 81%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満
実施例2	20% / 85%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満
実施例3	20% / 83%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満
実施例4	20% / 83%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満
実施例5	20% / 83%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満
実施例6	20% / 81%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満
実施例7	20% / 83%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満
実施例8	20% / 81%	100時間以上	10%未満 / 10%未満	10%未満 / 10%未満

【0036】

【発明の効果】以上、詳細かつ具体的な説明から明らかなように、本発明により、Sb₃Te系記録材料相変化記録メディアの初期化レス製造を可能として、DVD-ROM互換が可能な4.7GB／直径120mmディスク以上の記録密度の初期化レスメディアを実現できるという極めて優れた効果を奏するものである。

【図面の簡単な説明】

【図1】本発明による光情報記録媒体の一例を示した図である。

【図2】本発明による光情報記録媒体の一例を示した別の図である。

【図3】本発明による光情報記録媒体の一例を示した更に別の図である。

【図4】本発明の光情報記録媒体への記録モードの1例を示した図である。

【符号の説明】

1 基板

2 第1の誘電体層

3 結晶化促進層

4 記録層

5 第2の誘電体層

6 反射放熱層

7 保護層

8 基板

40 9 第1の誘電体層

10 結晶化促進層

11 第1の記録層

12 第2の誘電体層

13 半透明反射放熱層

14 保護層

15 第3の誘電体層

16 第2の記録層

17 結晶化促進層

18 第2の誘電体層

50 19 反射放熱層

(7)

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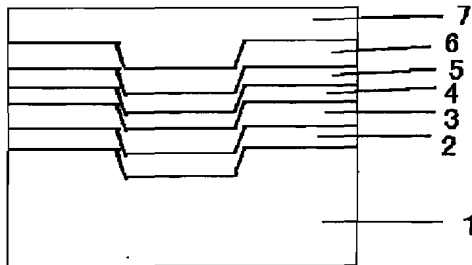
12

20 基板
21 カバー層
22 第1の誘電体層
23 結晶化促進層
24 第1の記録層
25 第2の誘電体層
26 保護層

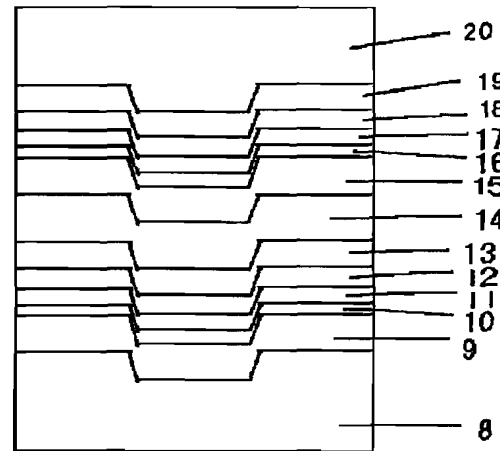
* 27 第3の誘電体層
28 第2の記録層
29 結晶化促進層
30 第4の誘電体層
31 反射放熱層
32 基板

*

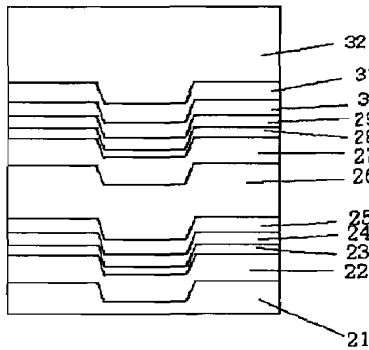
【図1】



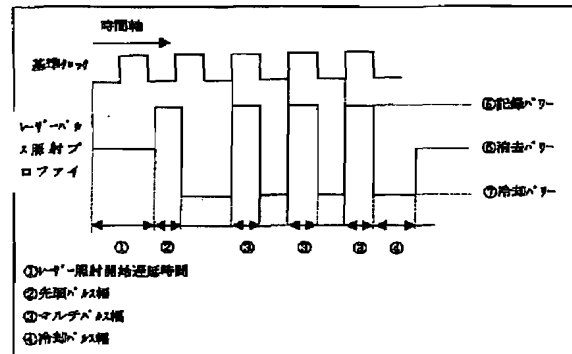
【図2】



【図3】



【図4】



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